

Anodic carbon oxidation in molten carbonate:

Why molecular mechanisms may be less relevant than wetting behavior

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Outline

- 1. Introduction
- 2. Processes on nm and μm -to-mm scale: MCFC electrodes
- 3. Processes on nm and μm -to-mm scale: DCFC anode
- 4. Molecular reaction mechanisms?
- 5. Dynamic interaction between nm and μm -to-mm processes?
- 6. Research priorities

1. Introduction

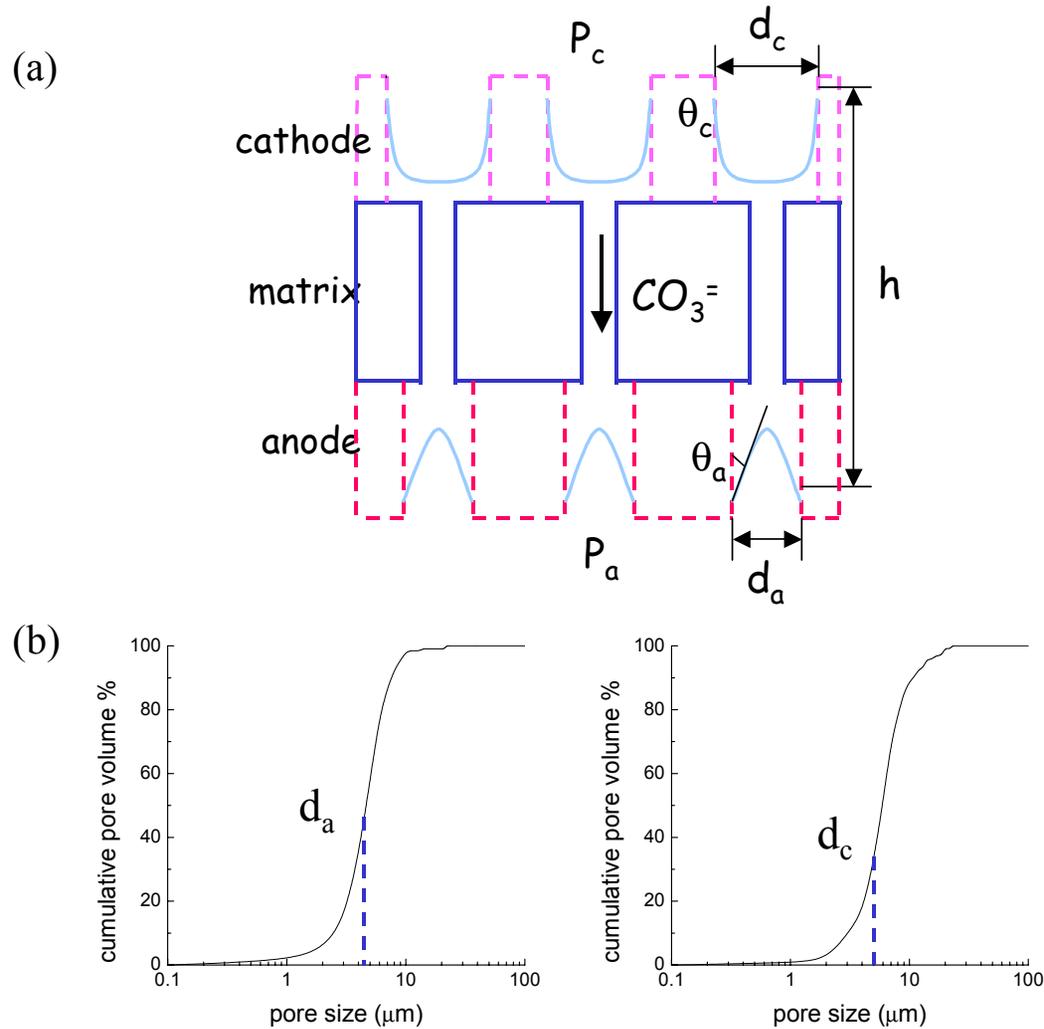
- 1. Fuel cell electrode optimization:
 - Why? Increase power density
 - Factors limiting scale-up
 - How? Accelerating kinetics
 - Balancing active area vs reactant supply
 - Well-defined ranges porosity, pore and particle size
- 2. What we know about the DCFC anode on lab scale
 - OCV erratic and anode-gas-dependent
 - Polarization quasi-linear, not strongly surface or particle-size dependent
 - Maximum power density 50-100 mW/cm²
 - Reaction product CO₂, not CO as partly expected

2. Processes on nm and μm -to-mm scale: MCFC electrodes

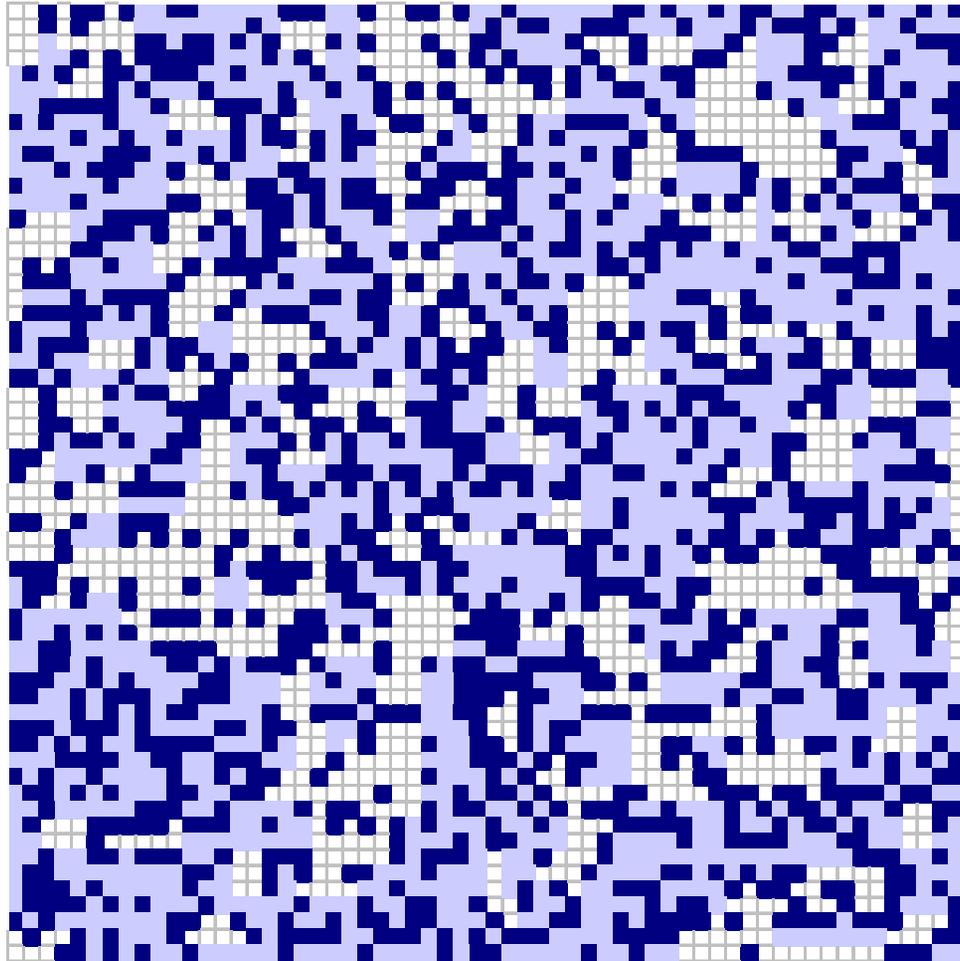
On μm -to-mm scale:

- Fixed 3-phase contact zone is focus of reaction
- Extent of reaction zone limits performance when kinetics slow (cathode) \rightarrow active area to be maximized
- Solid structure (electrocatalyst) makes this easy: key is melt and gas distribution over pore spectrum
- Gas phase transport not usually limiting (compare DCFC anode: product gas forms “pores”!)

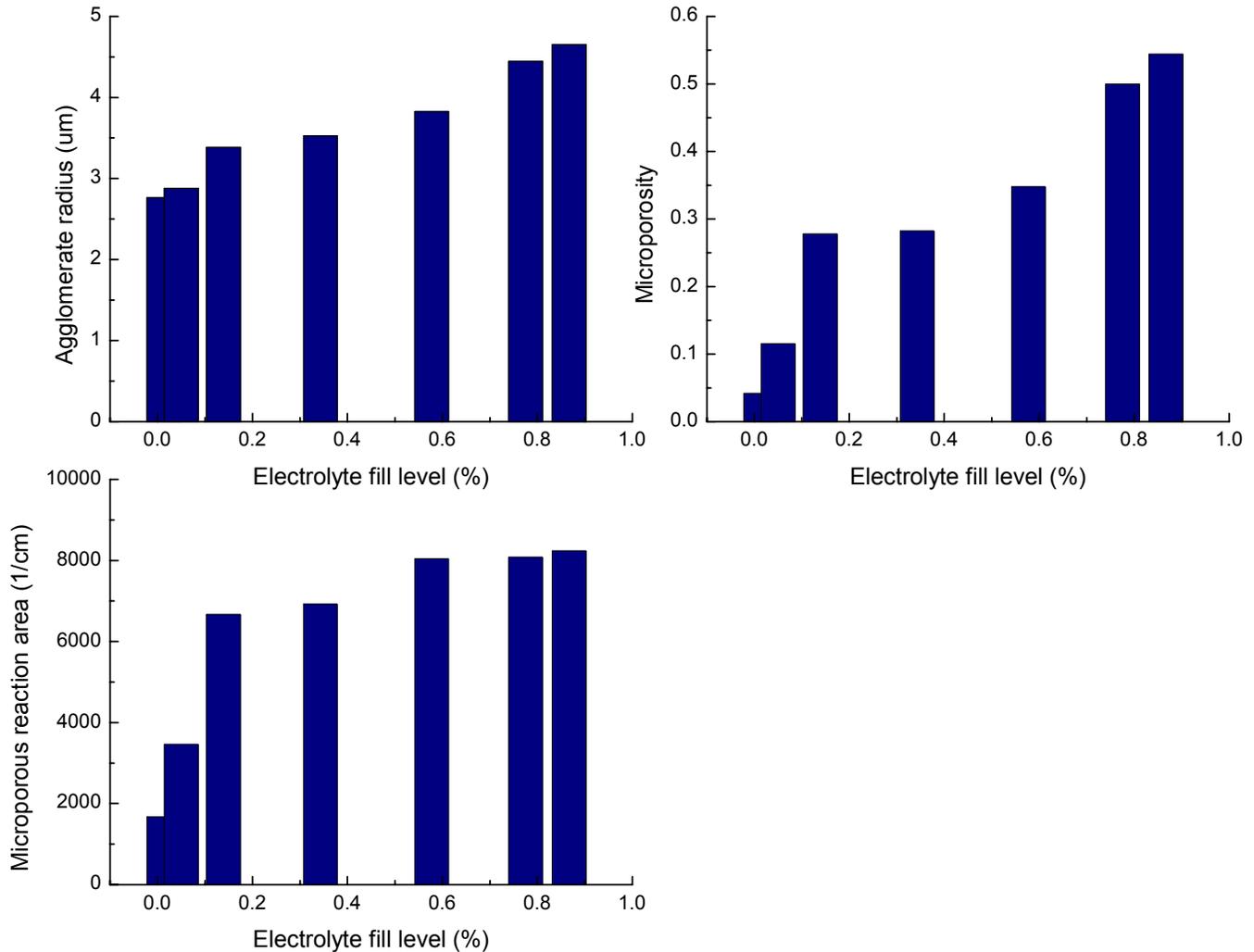
Wetting angle and critical pore size



Electrolyte Distribution and Electrode Fill Level



Effect of electrolyte fill level on agglomerate structure parameters



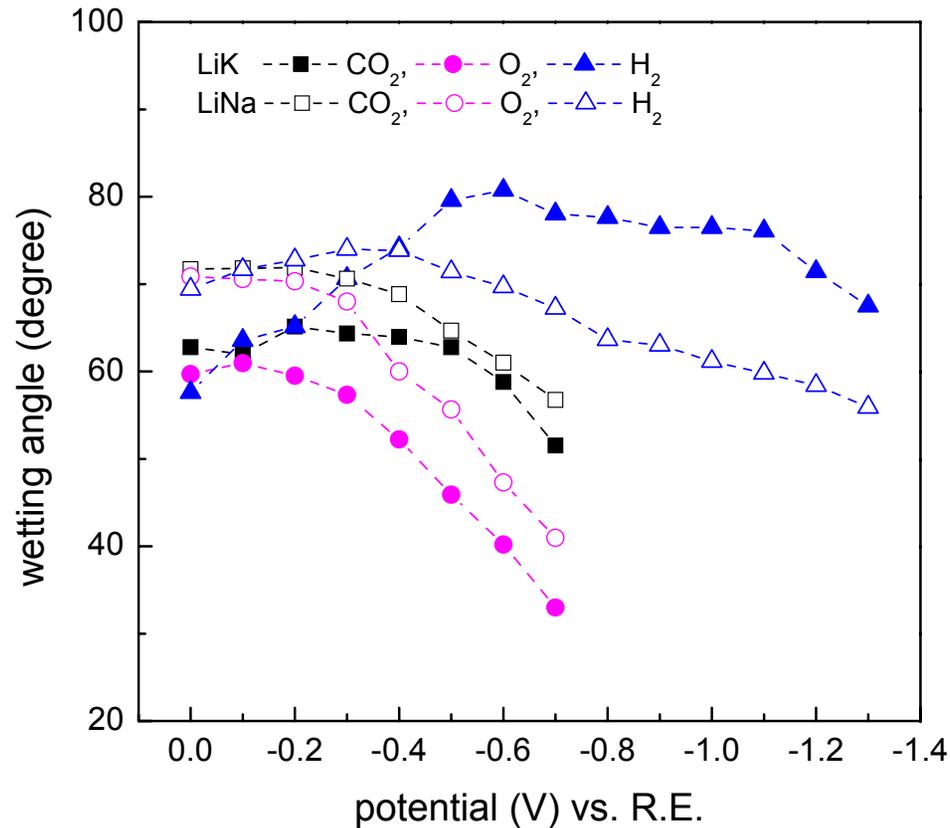
2. Processes on nm and μm -to-mm scale: MCFC electrodes (continued)

On nm scale, investigation difficult, but:

Indirectly, wetting studies have given some insight:

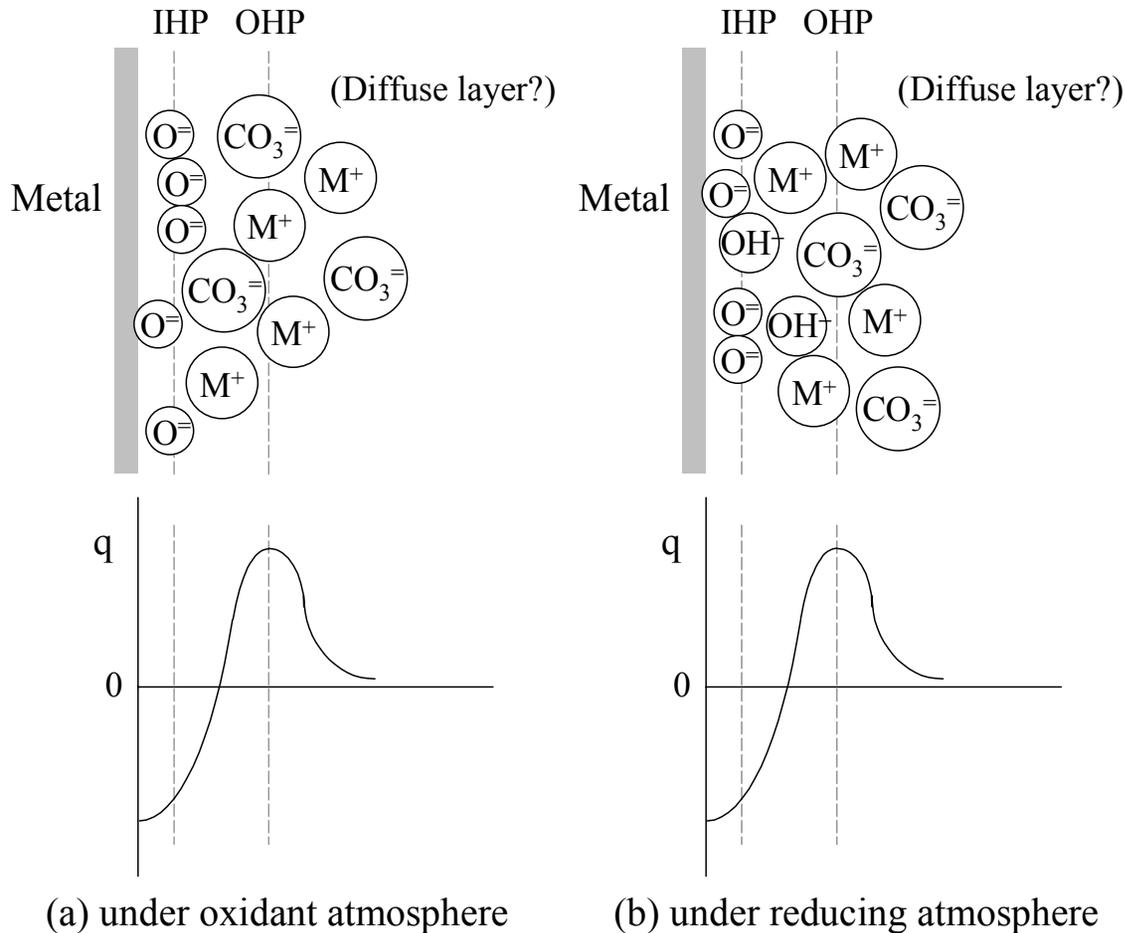
- Oxide ion (O^{2-}) strongly adsorbed at metals, and present at high surface concentration (relative to bulk). Adsorbed oxide species probably key in practical electrode process (oxide)
- In the cathode, O_2 and CO_2 are condensed to carbonate
→ strong role of wetting in electrocatalysis by oxides, but also at high load local deactivation or reaction oscillations
(Note: in DCFC anode under high load, opposite may occur: disappearance of carbonate and drying up of underlying substrate)

Wetting angle under polarization



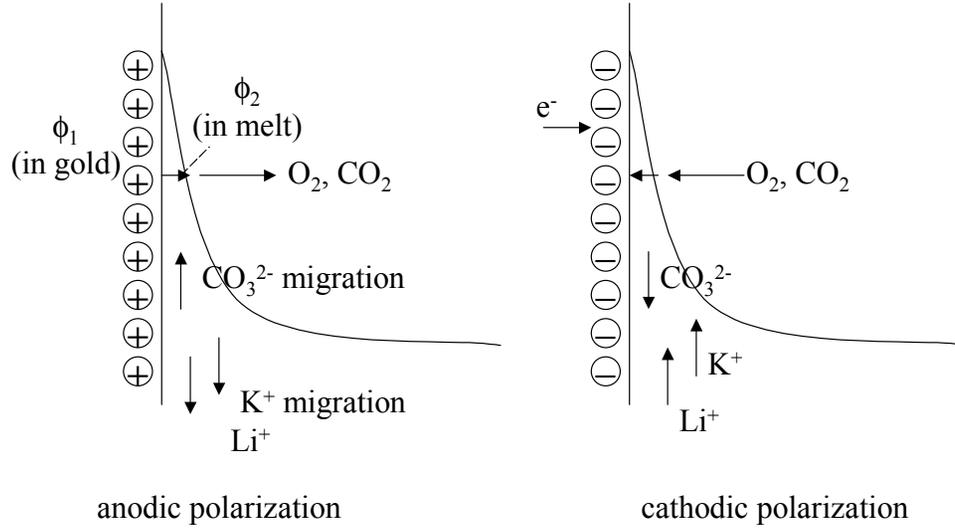
Wetting angle in Li-K and Li-Na melts, at 650°C and 1 atm

Double layer structure and charge profile

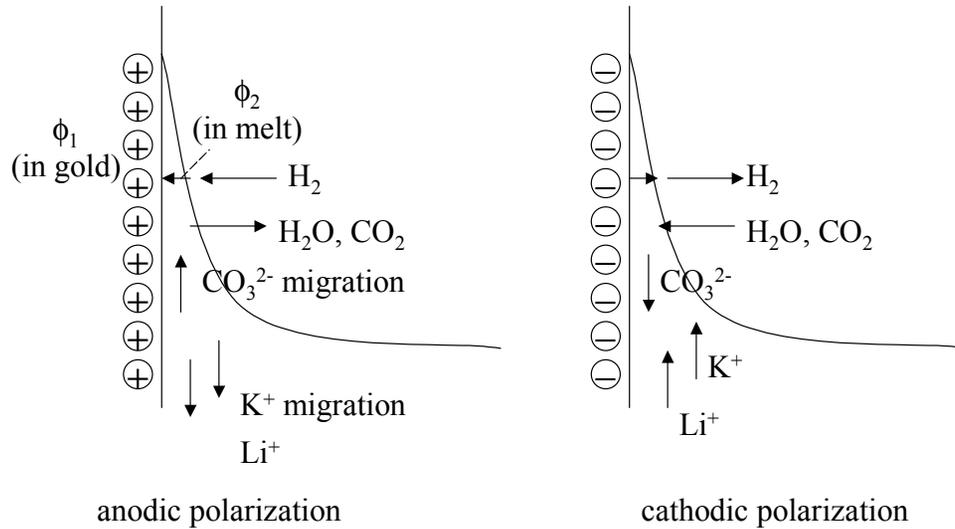


Electric double layer structure at a metal electrode in molten carbonate, and charge profile in the double layer. M^+ indicates alkali ions (Li^+ , K^+ , Na^+).

(a) under oxidant atmosphere



(b) under reducing atmosphere



Schematic of electrode and transport processes in the meniscus at a MCFC electrode.

3. Processes on nm and μm -to-mm scale: DCFC anode

On nm scale:

Expect even stronger O^{2-} adsorption at carbon than at metals

Adsorption strength \sim oxides such as LiCrO_2 , $(\text{Li}_x)\text{NiO}$ and LiCoO_2

Strong oxide adsorption identified early (Janz et al. 1960s: strong hysteresis in electrolysis carbonate to C or CO)

On μm -to-mm scale,

Moving 3-phase boundary, due to CO_2 (and some CO) production

CO_2 initially dissolves, but in a stationary process evolves bubbles

Bubbles cause (1) convection, (2) stochastic separation/contacting of particles (pulsating convection) \rightarrow fluidized bed characteristics, but: gas evolution causes the fluidization!

Interfacial interactions or reaction mechanism?

What explains the observed characteristics of the DCFC anode?

(Insensitivity of polarization to type, size, and surface area of carbon; anomalous production of CO₂)

Is it a result of

- molecular-level reaction mechanisms?

Or can it be explained by

- interaction of interfacial processes at the nm and the μm -to-mm scale?

4. Molecular-level reaction mechanisms?

Reaction mechanisms in literature are based on Hall process (cryolite melt containing some oxide → largely acidic chemistry).

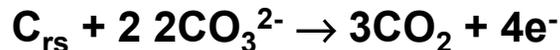
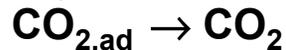
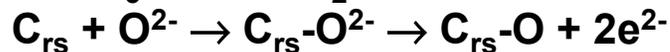
Of special interest: Haupin-Frank (ALCOA)

(a) Release of O^{2-} by decomposition of complex fluoaluminate ions $[Al_2O_2F_4]^-$



(b) Formation of C-O-C (“C₂O”) bridges between reactive-site C atoms on the exposed C surface, then extended to C-O-C-O-C (“C₃O₂”) bridges. These become unstable and release CO₂ by cutting of edge C-O bonds.

A variant of this for molten carbonate has been proposed by Cooper(LLNL):



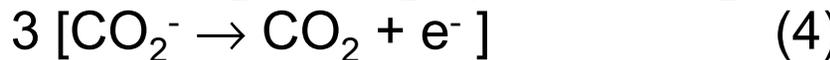
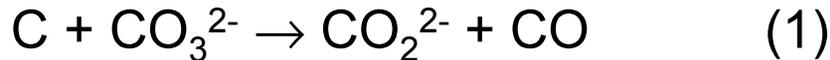
Molecular-level reaction mechanisms (cont'd)

3. Reactive intermediates in the melt:

CO oxidation in carbonate (Appleby and Borucka) may take place via intermediate CO_2^{2-} ion.

Instability of this ion accounts for slowness of CO oxidation.

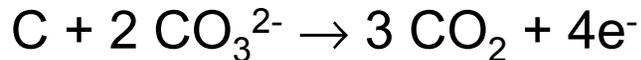
Applying to C oxidation:



Note: (1+2) may be slow

Fast equilibrium, strongly left

Fast \rightarrow displaces (3) to right



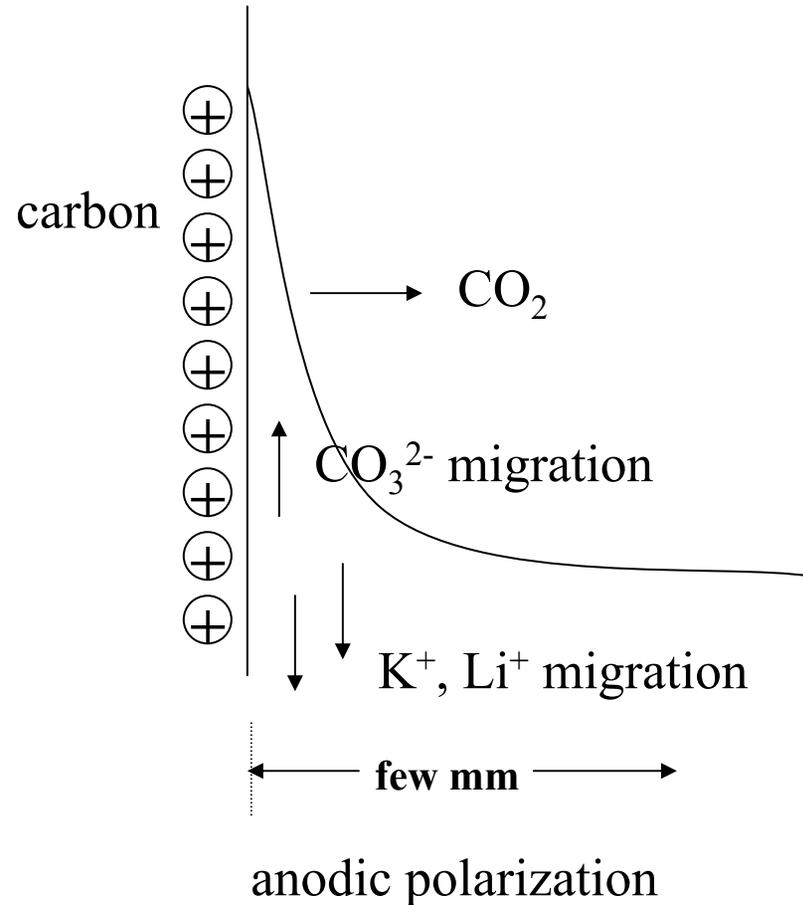
This mechanism makes use of single-electron transfer steps only.

5. Dynamic interaction of processes at nm-scale and μm -to-mm scale?

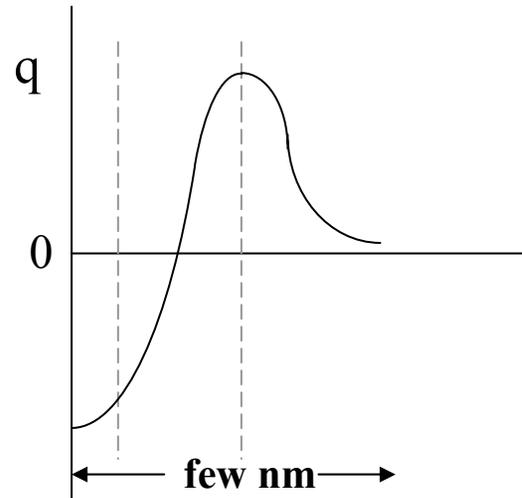
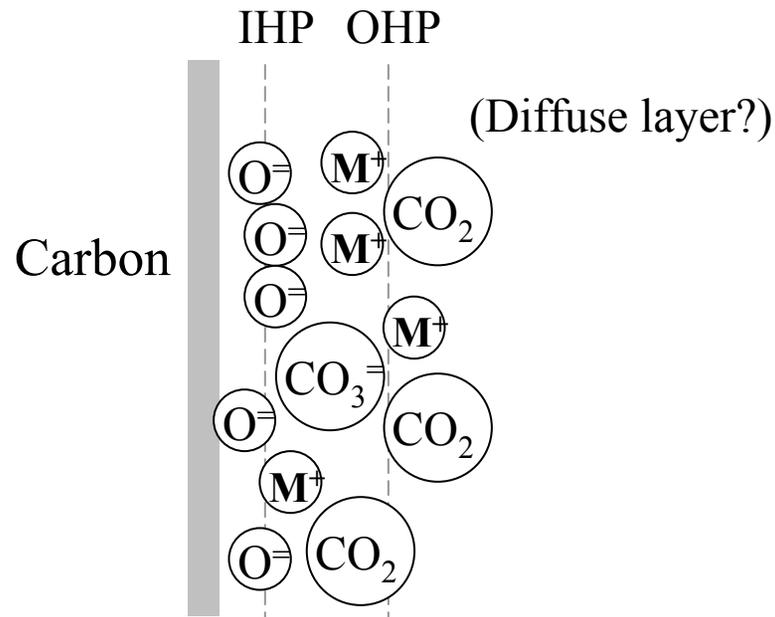
- nm-scale: specific adsorption of ions from melt on carbon surface (inner Helmholtz plane, IHP) is very strong
 - 1. Relative surface concentration O^{2-} at IHP \gg bulk concentration ,
 2. Due to dissociation equilibrium, CO_2 more rich in outer part of electric double layer or diffuse layer
- μm -to-mm scale: contacting carbon particles are covered partly by a μm -thin layer of molten carbonate through which gas is produced, but:
 - reaction zone near particle contact is displaced by growing interstitial gas bubble (of final size commensurate particle size)
- at the interface of carbon, electrolyte layer, and gas bubble, CO and/or CO_2 development continuously thins, and pushes back, the electrolyte layer until the resulting bubble is large enough to escape

Schematic of electrode and transport processes

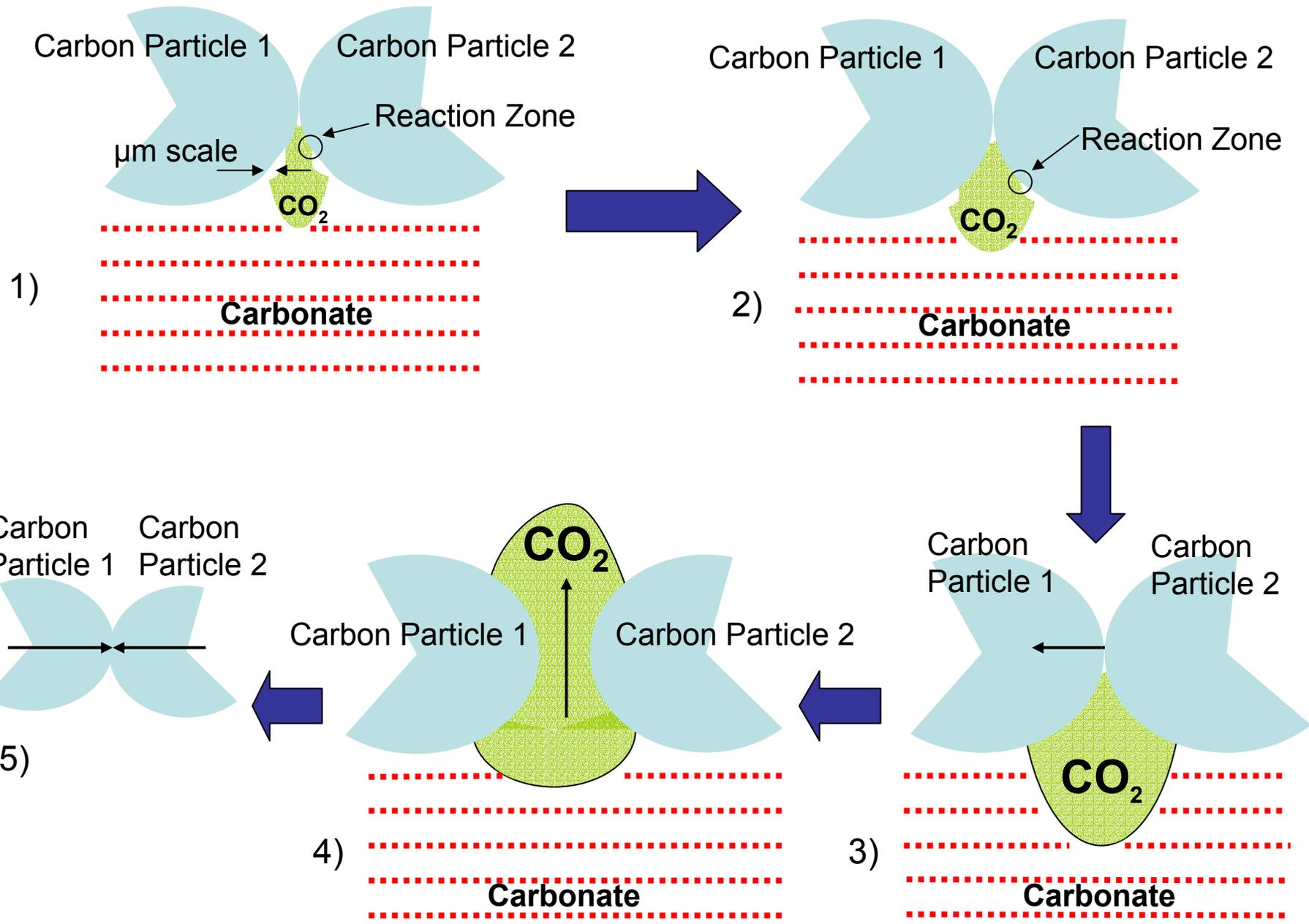
under CO₂ atmosphere



Double layer structure and charge profile



under CO_2 atmosphere



Characteristics of the μm -to-mm scale process

- Pulsating convection (stochastic but average roughly periodic, at constant load)
- Fluidized-bed-like pulsation is primary reason for insensitivity of performance (at constant load) to size and surface area of the carbon particles
- Primary frequency of this pulsation, and primary bubble size, is determined by the wetting tendency of the electrolyte at carbon and the current being passed (volumetric gas evolution rate)

Characteristics of the nm-scale process

- Tendency of carbonate melt to wet carbon (especially under load) in DCFC anode is a rate process determined by molecular-level forces.
- Rate of wetting at the 3-phase contact edge depends on balance between (1) attraction of O^{2-} ions in the liquid-gas interface to the fresh carbon surface exposed by oxidation of over-layers; (2) strength of residual O^{2-} adsorption on surface wetted by melt but yet unoxidized
- This balance must be largely dependent on the melt chemistry, and on the degree of (molecular) disorder of the carbon surface, but not on particle size

The nm-scale process, interacting with μm -to-mm scale pulsation, may explain CO_2 formation

- Strong tendency to dissociation of carbonate at carbon (preferential adsorption of O^{2-} ions in the IHP, and CO_2 concentration near edge of double layer)
→ can this interact with single-electron-step CO formation?

Hypothesis:

Any electron-transfer process at the IHP in which O^{2-} ions are continuously consumed and CO is produced (by whatever route), results in strong tendency, within the EDL, to establish Boudouard-type equilibrium between CO_2 and CO.

- If this reasoning is correct, there is no need for a Boudouard step in the gas-phase to explain the 4- e^- oxidation of C.
- But needed to check: experimental data relevant to nm level!

6. Research Priorities (Technology Base)

1. Wetting characteristics of various types of carbon, in melts of variable basicity (cation composition, and OH⁻ added) and temperature
2. Spectroscopic characterization of molten carbonate in reducing medium, in contact with carbon, to establish identity of stable and semi-stable species
3. Molecular Dynamics (MD) calculations to establish the relative stability of carbon-carbonate-CO-CO₂ configurations in the melt
4. Monte-Carlo (stochastic) modeling of assemblies consisting of cells representing carbon particles, gas bubbles (CO₂, CO), and carbonate melt. Buoyant forces, interfacial forces, and electrochemical reactions to be accounted for, cell-to-cell